Properties and applications of metastable precious metal intermetallic compounds

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Certificate of original authorship

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

Supitcha Supansomboon

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The purpose of my precious journey was to investigate precious metal alloys and compounds. Throughout my journey, not only did I achieve this purpose, but also I gained far greater precious experiences and friendships here in Australia.

Table of Contents

Abstract

Precious metal alloys and compounds have myriad applications in the fast-expanding horizons of the commercial and industrial worlds. They are also fascinating topics for scientific research. These materials have a long history, with gold and silver amongst the very earliest metals used by humans. Over the past millennia, the primary applications of the precious metals and their alloys have been in the ever-lucrative jewellery manufacturing industry. The traditional alloys have been perfected in over three thousand years of experience. However, in the recent past, precious metal alloys and compounds have also found themselves a crucial place of pride in the burgeoning 'advanced materials' sector. Gold-based and platinum-based alloys and compounds are amongst the candidates being investigated for serving in those applications. In the present project I sought to explore how gold aluminide and platinum aluminide could be developed for further innovative applications. In particular, I initially became interested in the optical properties of these materials, with a view to developing their application in the jewellery industry. The Pt_xAl alloys are, however, also useful as precursors for producing nanoporous metal sponges. The availability of such samples from the first part of the project encouraged me to consider technological applications of the aluminides in the chemical catalysis industry in the second part of the project. The two parts are linked by virtue of starting with the same materials, which are fabricated and mostly characterized the same way. In both cases the samples are fabricated as thin films by direct-current magnetron sputtering and then various techniques are used to characterize their chemical composition, structures, morphologies and specific properties. The main difference comes only at the very end of each part, with the first group of materials being evaluated on their optical properties and the second on their sponge-forming properties.

My work is developed around two hypotheses. First, I hypothesized that the compounds $PtAl_2$ (brassy yellow) and $AuAl_2$ (metallic purple) can be alloyed to yield a range of intermediate colours. It is generally stated that these compounds would be immiscible but I proposed that a series of metastable solid solutions could be formed by means of magnetron sputtering. Secondly, I hypothesised that the preparation of nanoporous platinum sponges from metastable (Pt_xAl) precursors would produce a different result than producing them from well-crystallized precursors, and that this could be exploited to provide a new way to control the morphology of such sponges.

The work has showed that the attractive colours of the intermetallic compounds $AuAl_2$ ('purple gold') and $PtAl_2$ ('golden platinum') can be combined or mixed to produce an interesting colour spectrum. This may be of interest to the jewellery industry. A series of metastable solid solutions could be formed by using the magnetron sputtering technique, which enables users to produce any desired stoichiometry. In addition, procedures to reliably

produce pure $AuAl_2$ and $PtAl_2$ thin films have been established. These have lattice parameters of 0.599 nm and 0.594 nm respectively, which are similar to those of bulk samples produced by vacuum arc melting. Addition control may be obtained by designing multilayer stacks of these intermetallic compound films, with both bi-layer and multi-layer films being produced in the present project. It was also shown that a metastable solid solution of Au and Pt could be formed by sputtering, with a co-deposited film of 54 at.%Au- 46 at.%Pt film forming a solid solution with a lattice parameter of 0.401 nm, which lies between that of pure Au films (0.408 nm) and pure Pt films (0.394 nm). This metastable solid solution could be reacted with a pure Al film to form a metastable solid solution of $(Au,Pt)Al_2$ after annealing. However, thin film stacks of $AuAl_2$ and $PtAl_2$ may be a better choice to tune colours of these two compounds as they are easier to control.

Next I showed that Pt-Al alloys and intermetallic compounds can be de-alloyed in alkaline solutions to produce nanoporous platinum sponges. These nanoscale sponges can be used as chemical catalysts although I did not pursue this aspect myself. Rather, in this part of the project I considered how the microstructure of the precursor alloys could control the morphology of subsequent sponges. Once again, metastable precursors could be prepared by using magnetron sputtering, and produced a different morphology of sponges compared to those produced from well-crystallized precursors. Other processing parameters have also been studied. It was found that mole fraction (χ_{Al}) of Al in the precursor and the deposition temperature are the two most important factors. Precursors with $\chi_{Al} < 0.60$ did not form sponges after either deposition at elevated or room temperature. 'Mud-cracked' mesoporous sponges could be formed by preparing precursors with $\chi_{Al} =0.67$ and deposited at elevated temperature. The Pt_8Al_{21} and meta-stable phase (ε-phase) were formed in precursors with $0.67< \chi_{Al} < 0.90$ that had been deposited at elevated temperature. In this case de-alloying produced classic isotropic fibrous sponges. Disordered and fragile masses were obtained when precursors with $\chi_{Al} > 0.90$ were de-alloyed. These had originally consisted of a mixture of $PtAl_6$ and pure Al. It was also found that precursors that had been deposited at room temperature produced very different sponge morphologies to those that had been deposited at elevated temperature: in this case the amorphous precursors with $0.67 < \chi_{Al} <0.96$ produced sponge morphologies ranging from pinhole to unusual isotropic foamy. This work has shown that different morphologies of nanoporous platinum sponges can be produced by controlling the processing parameters. These sponges might be considered for use in specific catalytic or sensor applications because they can be fabricated using simple and cost-effective production techniques.

Publications and conference presentations arising from this work

Publications

1. Supansomboon, S., Bhatia, V., Thorogood, G., Dowd, A., and Cortie, M.B., Advanced precious metal alloys, *Materials Australia*, 2011. 44 (4): p.41-46.
2. Keast, V.J., Birt, K., Koch, C.T., Supansomboon, S., and Cortie, M.B., The role of plasmons and interband transitions in the color of $AuAl_2$, $AuIn_2$, and $AuGa_2$. *Applied Physics Letters*, 2011. **99**(11): p. 111908.
3. Keast, V.J., Zwan, B., Supansomboon, S., Cortie, M.B., and Person, P.O.Å., $AuAl_2$ and $PtAl_2$ as potential plasmonic materials. *Journal of Alloys and Compounds*, 2013. **577**: p. 581-586.
4. McPherson, D.J., Supansomboon, S., Zwan, B., Keast, V.J., Cortie, D.L., Gentle, A., Dowd, A., and Cortie, M.B., Strategies to control the spectral properties of Au–Ni thin films. *Thin Solid Films*, 2014. **551**: p. 200-204.
5. Supansomboon, S., Porkovich, A., Dowd, A. Arnold, M.D., and Cortie, M.B., Effect of precursor stoichiometry on the morphology of nanoporous platinum sponges. *ACS Applied Materials & Interfaces*, 2014. **6**(12): p. 9411-9417.
6. Supansomboon, S., Dowd, A., Lingen, E. van der, Keast, V.J., and Cortie, M.B., Coatings of coloured intermetallic compounds for decorative and technological applications, *Materials Forum* (accepted, 2014).
7. Supansomboon, S., Dowd, A., Gentle, A., Keast, V.J., Lingen, E. van der, and M.B. Cortie, Thin films of $PtAl_2$ and $AuAl_2$ by solid-state reactive synthesis (being prepared for submission).

Conference presentations

1. Supansomboon, S., Dowd, A., and Cortie, M.B., Phase relationships in the $PtAl_2$-$AuAl_2$ system, *35th Condensed Matter and Materials Meeting*, 1-4 February, 2011 Charles Sturt University, Wagga Wagga, New South Wales, Australia. (Poster presentation)

2. Supansomboon, S., Dowd, A., and Cortie, M.B., Optical properties of nanoscale bi-layers of the coloured intermetallic compounds Al_2Pt and Al_2Au, *the 10th Asia-Pacific Microscopy Conference (APMC10), the 2012 International Conference on Nanoscience and Nanotechnology (ICONN2012) and the 22nd Australian Conference on Microscopy and Microanalysis (ACMM22)*, 5 – 9 February 2012, the Perth Convention & Exhibition Centre, Western Australia, Australia. (Poster presentation)

3. Supansomboon, S., Dowd, A., and Cortie, M.B., Thin film stacks of the colored intermetallic compounds Al_2Au and Al_2Pt, *Gold 2012*, 5-8 September 2012, Keio Plaza Hotel Tokyo, Tokyo, Japan. (Poster presentation)

4. Supansomboon, S., Dowd, A., and Cortie, M.B., Colored intermetallic compounds for gems and jewelry application, *The 3rd International Gem and Jewelry Conference*, 12-16 December, 2012, the Imperial Queen's Park Hotel, Bangkok, Thailand (Oral presentation)

5. Supansomboon, S., Dowd, A., and Cortie, M.B., Coatings of coloured intermetallic compounds: $AuAl_2$ and $PtAl_2$ for decorative and technological applications, *Materials Innovation in Surface Engineering*, 19-21 November 2013, University of South Australia, Adelaide, South Australia, Australia (Oral presentation)

6. Supansomboon, S., Gentle, A., Dowd, A., and Cortie, M.B., Nanoscale bi-layers of coloured intermetallic compounds, *Australian Nanotechnology Network Early Career Workshop*, 10-11 July 2014, University of Technology, Sydney, New South Wales, Australia. (Poster presentation)

7. Supansomboon, S., Dowd, A., and Cortie, M.B., Formation of nanoporous platinum sponges by de-alloying Al_xPt, *The 3rd Biennial Conference of the Combined Australian Materials Societies (CAMS 2014)*, 26-28 November 2014, Charles Perkins Centre, University of Sydney, New South Wales, Australia. (Oral presentation)

List of Figures

List of Tables